Applied Energy 133 (2014) 282–288

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Promoting effect of various biomass ashes on the steam gasification of low-rank coal

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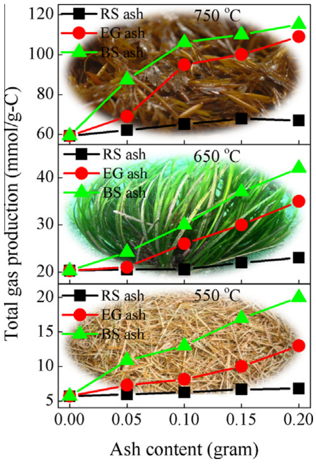
HIGHLIGHTS

- Biomass ash was utilized to promote gasification of low rank coal.
- Promoting effect of biomass ash highly depended on AAEM content in the ash.
- Stability of the ash could be improved by maintaining AAEM amount in the ash.
- Different biomass ash could have completely different catalytic activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form 27 June 2014
Accepted 24 July 2014
Available online 17 August 2014

Keywords:
Biomass ash
Alkali and alkaline earth metal
Low rank coal
Steam gasification
Stability

ABSTRACT

Application of biomass ash as a catalyst to improve gasification rate is a promising way for the effective utilization of waste ash as well as for the reduction of cost. Investigation on the catalytic activity of biomass ash to the gasification of low rank coal was performed in details in the present study. Ashes from 3 kinds of biomass, i.e. brown seaweed/BS, eel grass/EG, and rice straw/RS, were separately mixed with coal sample and gasified in a fixed bed downdraft reactor using steam as the gasifying agent. BS and EG ashes enhanced the gas production rate greater than RS ash. Higher catalytic activity of BS or EG ash was mainly attributed to the higher content of alkali and alkaline earth metal (AAEM) and lower content of silica in it. Higher content of silica in the RS ash was identified to have inhibiting effect for the steam gasification of coal. Stable catalytic activity was remained when the amount of AAEM in the regenerated ash was maintained as that of the original one.

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http://dx.doi.org/10.1016/j.apenergy.2014.07.091
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1. Introduction

Gasification is a thermochemical conversion process in which solid carbonaceous materials such as coal and biomass are converted into syngas. Recently, gasification process has been intensively studied to produce syngas from alternative and renewable fuel such as woody biomass and agricultural residues [1–5]. Gasification is also considered as an effective way to utilize coal cleanly. Despite the serious environmental problem by burning coal, coal is still widely used and becomes the main energy sources in the world due to its low-cost. It shared about 29.9% of global primary energy consumption in 2012 in which China, USA and India shared approximately 50.2%, 11.7% and 8.0%, respectively [6]. The main purposes to develop the coal gasification technology are to increase the conversion efficiency [7–11] and to utilize low-rank coal effectively [12–16].

Utilization of catalyst to increase the gasification rate is an attractive option. It can either increase the coal conversion rate at certain temperature or decrease gasification temperature but maintain the high conversion rate [17,18]. Furthermore, the use of catalyst can reduce the tar formation [19,20]. Sutton et al. [21] summarized the fundamental criteria for the selection of catalyst for the gasification. The selected catalyst should be able to remove tar effectively, to reform methane well, and to obtain the intended syngas ratio. Furthermore, the catalyst should not be easily deactivated, or can be easily regenerated, and has low cost. Some catalysts such as nickel based catalysts were found to be able to increase the hydrogen production, and result in a high H_2/CO ratio [22]. Some natural minerals such as olivine [23], calcite [24], and dolomite [25] were also found to be suitable for the gasification. Alkali and alkaline earth metal (AAEM) species have been extensively applied for the coal gasification due to their high catalytic activity and low cost [26–31]. Mitsuoka et al. [26] investigated the catalytic effect of K and Ca on the CO_2 gasification of Japanese cypress char and the result confirmed that the additions of K and Ca effectively enhanced the reactivity of char. K and Ca species were also found to improve the reactivity of coal char [27]. Zhang et al. [29] successfully utilized low cost AAEM precursors such as soda ash and slaked lime for promoting the pyrolysis of coal char. In fact, almost all biomass contain AAEM species. However, different biomass contains different contents of AAEM. Biomass with high content of AAEM was found to be able to improve the gasification performance when it was co-gasified with coal [32–37] or with other biomass containing low concentration of AAEM [38]. It is found that some components of AAEM in the biomass were easily volatilized and resulting in the increase in the reactivity of the coal [36,37]. When biomass is burnt, most of AAEM species could still remain in its ash. The cost will be considerably reduced if biomass ash can be used as the catalyst. Biomass ash was found to be able to promote the biodiesel production rate due to its alkalinity [39–42]. Ash was also reported to have good catalytic activity for other reactions such as ethanol dehydrogenation [43] and partial oxidation of methanol [44]. Lahijani et al. [45] successfully used the ash from palm empty fruit bunch to enhance CO_2 gasification of palm shell char. However, only limited number of studies focused on the direct utilization of biomass ash for promoting coal gasification rate. In the present study, various biomass ashes were prepared at different calcination temperatures and used for the gasification of low-rank coal. The effects of the ash compositions and ash addition amount in the coal sample on the gasification rate were investigated in details. To understand the effect of AAEM contents in the ash on the catalytic activity, simulated catalysts, i.e., K/CaO and K/SiO_2 with different K loading amounts, were prepared and used for the coal gasification. The stability and reusability of the ash as the catalyst were also examined in order to provide more information for the application biomass ash as a catalyst in a practical gasification process.

2. Materials and methods

2.1. Feedstock and ash preparation

Adaro coal (Indonesian brown coal) is a kind of low rank coal. Proximate analysis result based on ASTM S3172-75 and ultimate analysis result based on elemental analyzer (Vario EL cube elemental analyzer) for it are shown in Table 1. It was ground and sieved to particle size of 1–2.8 mm and dried in the oven at 105 °C overnight prior to use. The remaining moisture content was measured by using moisture content analyzer (MX50, AND, Japan).

Three kinds of biomass (rice straw, eel grass/*Zostera caespitosa*, and brown seaweed/*Sargassum horneri*) collected from Aomori Prefecture, Japan were chosen as the ash sources since they contained high content of ash as shown in Table 2. Ash contents of rice straw (RS), eel grass (EG), and brown seaweed (BS) were 14, 6.6, and 13.5 wt% in dry base, respectively. In order to investigate the effect of calcination temperature on the ash catalytic activity, various ashes were prepared by calcination of biomass at 600, 800, and 1000 °C for 2 h, respectively. Metal content in the ash was measured by using X-ray fluorescence (XRF) analysis (Energy Dispersive X-ray spectrometer, EDX-800HS, Shimadzu).

To understand the effect of AAEM content in the ash on the catalytic activity, two simulating catalysts, i.e., K/CaO and K/SiO_2, were prepared by incipient wetness impregnation method. Herein, Mg was assumed to have the similar effect as Ca since they have similar chemical properties as they are belonged to the same group. CaO support was obtained by calcining scallop shell at 1000 °C while SiO_2 was provided by Saint-Gobain Norpro, US. X ray diffraction analysis (XRD) showed that almost pure CaO phase was obtained from the calcination of scallop shell at 1000 °C. Catalyst support was soaked into the KNO_3 (Wako, Japan) solution at certain concentration so that the as-prepared catalysts would have the similar potassium composition as those in biomass ash (30 wt%-K/CaO for BS ash and 50 wt%-K/SiO_2 for RS ash). The slurry was then dried overnight in the oven and calcined at 650 °C for 3 h.

2.2. Gasification experiments

Steam gasification experiment was conducted in a fixed bed reactor. Schematic illustration of the experimental setup can be

Table 1
Proximate and ultimate analysis of Adaro coal sample.

Proximate analysis (wt%-dry)			Ultimate analysis (wt%-daf)[a]			
Ash	Volatile matter	Fixed carbon[b]	C	H	O[b]	N
2.1	47.8	50.1	70.0	4.9	24.7	0.4

[a] Dry ash-free.
[b] By difference.

Table 2
Proximate analysis of brown seaweed, eel grass, and rice straw.

Biomass	Proximate analysis (wt%-dry)		
	Ash	Volatile matter	Fixed carbon[b]
Brown seaweed	13.5	52.8	33.7
Rice straw	14.0	52.0	34.0
Eel grass[a]	6.6	53.8	39.6

[a] Based on thermogravimetry analysis.
[b] By difference.

found elsewhere [36]. Stainless steel tube with an inner diameter of 16.5 mm and a length of 500 mm was used as the reactor. 1 g of coal feedstock was physically mixed homogeneously with certain amount of biomass ash (0.05, 0.1, 0.15, and 0.2 g). The ash was pelletized to a particle size of 0.5–0.8 mm (smaller than the coal particle size) to let it filled the void space between the sample. It was then loaded in the sample holder and put in the reactor. 50 cm^3/min of Argon was used as the carrier gas and 0.09 g/min of steam as the gasifying agent. The reactor was heated by electric furnace at a heating rate of 25 °C/min until the gasification temperature (550, 650, and 750 °C) was reached and then held at this temperature. The steam was introduced to the reactor from the beginning of heating. The total reaction time was fixed at 2 h for all experiments.

Steam and carrier gas was flown into the reactor from the top and volatile products were carried out from the bottom side. Volatile product was condensed using water–ice cold trap and the non-condensable gases passed through a gas purifier and were collected in a gas bag. The gas product was also collected from the beginning of heating until the experiment finished after 2 h. The collected gas was analyzed using a gas chromatograph (Agilent 7890A GC system, US) with two thermal conductivity detectors (TCD). One TCD was connected with three packed columns (2 molecular sieve 5A + 1 HayeSep Q columns) to detect and separate carbonaceous gas (CO_2, CO, and CH_4) and the other was connected with a molecular sieve 5A column to detect H_2. After the gasification reaction, the reactor was cooled down and the solid product in the sample holder was collected and weighted.

3. Results and discussion

3.1. Ash analysis

The ashes obtained by calcination of the three kinds of biomass at different calcination temperatures, i.e. 600, 800, and 1000 °C, should have different physical and chemical characteristics. Fig. 1a shows the ash yields at different calcination temperatures. For all biomass samples, the obtained ash amount decreased with the increase of the calcination temperature. The most significant decrease was found for the calcination of EG, where the ash yield was decreased from 13.7 wt% at 600 °C to 8.3 wt% at 800 °C and further decreased to 7.3 wt% at 1000 °C. In general, more volatiles will be generated and more carbon will be burnt out from the biomass at a higher calcination temperatures. Furthermore, some small ash particles, called fly ash, in which large amount of alkali and alkaline earth metal (AAEM) species are generally contained since some AAEM are easily volatilized, could be carried away by the flue gas stream [46,47]. As such, the amount of AAEM species in the remained ash will be decreased. It can be seen from Fig. 1b that the AAEM content of all ash samples decreased with the increase in the calcination temperature. On the other hand, some carbonaceous matters could be remained in the ash at lower calcination temperature. Visual observation of the ash indicated that some dark spots were found in the ash obtained at 600 °C but no dark spot was seen in the ash obtained at higher temperatures. It indicated that calcination of biomass at 600 °C for 2 h was not enough to burn out all the carbon in the biomass. In this study, for EG, the trace of carbon was obviously observed in the 600 °C ash but the carbon was completely disappeared when the calcination temperature was increased over 800 °C. This is the main reason why the ash yield of EG decreased sharply when the calcination temperature was increased from 600 to 800 °C. Furthermore, as shown in Table 3, the AAEM content in the 800 °C ash was still high, indicating that it is suitable to be used as the catalyst. Therefore, in this study, the ash prepared at 800 °C was chosen as the catalyst for the steam gasification of low-rank coal.

3.2. Effect of different biomass ashes on the gas production rate from coal

Fig. 2 shows the gas yield (in unit of mmol per gram carbon in dry coal sample) from the gasification of Adaro coal when 0.1 g of biomass ash was added to the coal sample. It is observed that the gas yield was increased to some extent when biomass ash was added into the coal sample. All biomass ashes showed catalytic activity for the coal gasification. However, the promoting effect on the gas yield was changed with the different ashes. It can be seen that the total gas yields were increased from 59.3 mmol/g-C to 94.8 and 106 mmol/g-C when EG and BS ashes were used respectively to assist the gasification at 750 °C, but the utilization of RS ash only improved the production rate to 65.2 mmol/g-C. Similar trend was also observed at the lower gasification temperature. At 650 °C, BS, EG, and RS ashes improved the gas yields from 20.3 mmol/g-C to 30, 26, and 20.5 mmol/g-C respectively and at 550 °C, the improvement was from 5.6 mmol/g-C to 8.4, 8.1, and 6.2 mmol/g-C, respectively. The different catalytic activities of the ashes should be mainly caused by the difference of AAEM content in the different ashes. As shown in Table 2, BS and EG ashes contain larger amount of AAEM. One can see that BS and EG ashes contain 77 and 72 wt% of AAEM (K_2O, CaO, and MgO), respectively while RS ash contains only 29 wt%. It is obvious that BS and EG ashes showed much higher catalytic activities than RS ash. Especially, it should be noted that the catalytic activity of BS ash was higher than that of EG ash since BS ash contains more potassium species (17.7 wt%) than EG ash (7.2 wt%). Zhang et al. [48] found that alkali metal (K and Na) had better catalytic activity than alkaline earth metal (Ca and Mg). It should be the main reason why BS ash promoted the coal gasification rate more than EG ash.

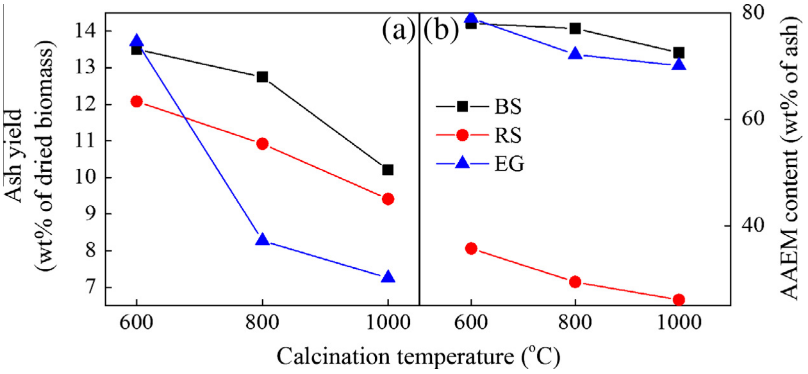

Fig. 1. Ash yield and AAEM content in various ashes obtained at various calcination temperatures; (a) ash yield and (b) AAEM content.

Table 3
Ash compositions of brown seaweed, eel grass, and rice straw after calcined at 800 °C for 2 h.

Component	Content (wt% of ash)			
	Brown seaweed	Rice straw	Eel grass	Adaro coal
SiO_2	n.d.	53.2	2.9	35.0
Al_2O_3	n.d	n.d.	n.d.	19.8
Fe_2O_3	0.4	2.4	2.9	21.4
CaO	34.2	2.6	49.1	11.5
MgO	25.2	n.d.	15.8	2.9
Na_2O	n.d.	n.d.	n.d.	0.3
K_2O	17.8	26.9	7.2	0.8
P_2O_5	2.5	2.4	2.6	0.1
TiO_2	n.d.	n.d.	0.1	1.1
SO_3	13.8	3.2	6.4	7.1
SrO	5.8	n.d.	0.5	n.d.
Cl_2O	n.d.	8.7	11.5	n.d.
MnO_2	n.d.	0.5	0.4	n.d.
Br_2O	0.2	0.0	0.4	n.d.
Rb_2O	0.0	0.0	0.0	n.d.
ZnO	0.2	0.0	0.1	n.d.
CuO	n.d.	0.0	0.0	n.d.

n.d. = not detected.

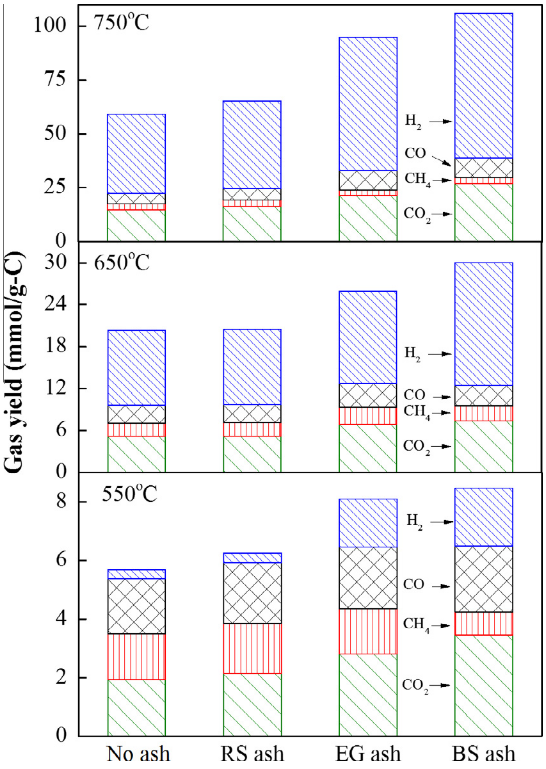

Fig. 2. Gas yields from the gasification of coal in the presence of various ashes (a) at 750 °C, (b) at 650 °C, and (c) at 550 °C.

On the other hand, RS ash was also found to have high content of potassium (26.8 wt%) which was even higher than that in BS ash (17.7 wt%). However, as shown in Fig. 2, the catalytic activity of RS ash was very low. It is possible that a high content of silica (53.2 wt%) which is also contained in the RS ash affects its catalytic activity. Dupont et al. [49] found that Si had an inhibitory effect on the gasification rate. Risnes et al. [50] indicated that Si in the form of silica could deactivate the catalytic activity of AAEM species by forming silicate, which has no catalytic activity. Therefore, the presence of potassium together with silica in the RS ash did not promote the gasification rate in the present study.

To confirm the role of metal compositions in the ash on the catalytic activity, BS and RS ashes were simulated by using man-made catalysts. Herein, potassium loaded calcium oxide (K/CaO) and potassium loaded silica (K/SiO_2) were prepared to simulate BS and RS ashes, respectively. The gasification was held at 750 °C so that the gas can be produced optimally and thus the role of the metal can be observed clearly. Gas yields from the coal gasification assisted by both of man-made catalysts are shown in Fig. 3. Comparing with the case without catalyst, as CaO was used, the gas yield increased to some extent. More gas was produced when potassium was loaded into CaO (Fig. 3a), indicating that the presence of both Ca and K resulted in higher catalytic activity. These results are in agreement well with those cases by using BS and EG ashes. On the contrary, as shown in Fig. 3b, the gas yield decreased when coal sample was mixed with silica only. As indicated by Dupont et al. [49], the presence of silica could inhibit the reactivity of the sample so that the gasification rate was decreased. Moreover, one can see that adding potassium to the silica gave almost no significant promoting effect on the gas yield. In the present study, when 30 wt%-K/CaO catalyst was used, the gas yield was increased from 59.3 to 90.7 mmol/g-C. However, even 50 wt%-K/SiO_2 was used, the gas yield was only increased from 59.3 to 66.4 mmol/g-C. It indicated that silica had great inhibitory effect on the catalytic activity of potassium. Therefore, even though RS ash contained higher amount of potassium, it did not catalyze the gasification rate as good as other ashes.

3.3. Effect of the biomass ash amount on the gas production rate from coal

In the practical process, it is important to understand how large amount of catalyst should be introduced into a gasifier so that all the coal can be gasified completely. In this study, the effect of the ash amount on the gasification rate was investigated at various gasification temperatures. As shown in Fig. 4, the total gas yield increased linearly along with the increase of BS ash amount when gasification was carried out at low temperatures (Fig. 4c for 550 °C and Fig. 4b for 650 °C). Similar results were also found for EG ash. However, when the gasification temperature was increased to 750 °C, a different increasing pattern was observed (Fig. 4a). Gas yield was increased sharply when the ash amount was increased from 0 to 0.1 g, and then the yield was increased very slowly when the ash amount was increased over 0.2 g. In the present study, coal particle size was kept at a constant, and in this case, a saturated contact area between the coal and the ash should be existed. If the coal contacted with the ash can be effectively gasified, especially at high gasification temperatures, adding more ash could not further enhance the conversion rate. Therefore, the trends as shown in Fig. 4 (a) for EG and BS ashes were observed. Similar results were also obtained by Lahijani et al. [45]. They found that the reactivity of char was improved when biomass ash was loaded on it. The increasing trend was found for ash content variation from 5 wt% until 10 wt%. However, the trend was not followed by continuous increasing the content to 12.5 wt%.

On the other hand, in any cases when RS ash was used, no significant increase of gas yield was observed even when the ash amount was increased. In general, larger amount of ash provides larger amount of AAEM and thus more active sites will be provided for the catalytic gasification of the coal. However, for the silica or silica-contained ashes, the aggregation of ash particles could occur on the coal surface more easily so that the total active surface area of the coal sample was decreased, resulting in the decrease of its reactivity [51,52].

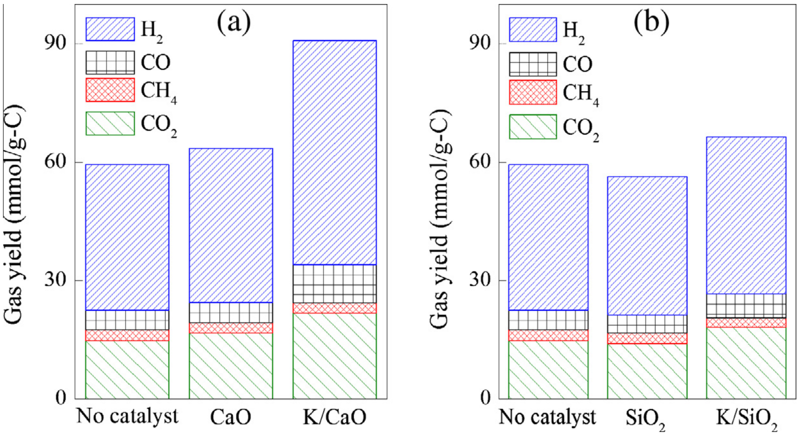

Fig. 3. Gas yields when potassium loaded catalysts were used (a) CaO support and (b) SiO$_2$ support.

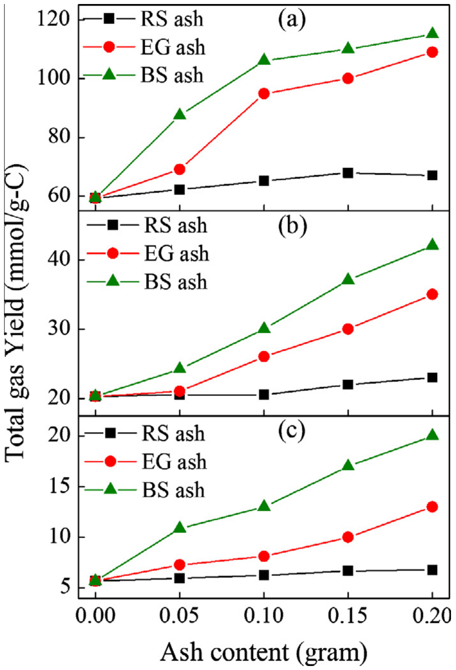

Fig. 4. Total gas yield as the function of ash amount in the mixture feedstock at various temperatures; (a) 750 °C, (b) 650 °C, and (c) 550 °C.

3.4. Reusability of biomass ash as catalyst

As stated above, in the present experiment, biomass ash was mixed physically with the coal sample. Compared with the impregnation method, physical mixing has less contact intensity between the coal sample and the catalyst. However, solid catalysts applied for gasification by physical mixing could be recovered and reused again after regeneration.

To test the stability and reusability of the ash, the recovery and regeneration were performed for the used ash. Solid product after the gasification which contained the mix of coal char and biomass ash was calcined at 800 °C for 2 h to remove the remained char so that biomass ash could be recovered. It should be noted that 2.1 wt% ash was also contained in Adaro coal as shown in Tables 1 and 3. Hence, the recovered ash contained the ash from the coal. This is the same as a practical gasification process. Since some of the ashes were lost during the gasification and calcination, in this study, as indicated in Table 4, certain amount of fresh biomass ash was added to the recovered ash so that total amount of the ash was remained at 0.1 g (the same as the original amount). Here, it was named as the regenerated ash.

Table 4
The amount of fresh ash added in each regenerated ash.

	Fresh ash added (g)		
	1st reg	2nd reg	3rd reg
Ash amount maintained			
BS ash	0.042	0.045	0.038
EG ash	0.012	0.018	0.015
AAEM amount maintained			
BS ash	0.065	0.061	0.059
EG ash	0.031	0.039	0.034

Stability and reusability test results for BS and EG ashes are presented in Fig. 5. Gas yield from the gasification assisted by the regenerated ash was observed, which is still much higher than that from the gasification without the ash assistance. It means that the ash was reusable since the catalytic activity of regenerated ash was still high. However, the catalytic activity of the regenerated ash was observed to be lower than the fresh one. The slight decrease of the gas yield was mainly caused by the decreasing of AAEM content in the regenerated ash because they are easily evaporated during gasification as well as regeneration processes. It is found that approximately 50–60 wt% of the original BS ash and 80–90 wt% of original EG ash including the coal ash can be recovered in the present study. Since there is silica in the coal ash, the amount of silica in the regenerated ash became higher, resulting in that the catalytic activity of the recovered ash decreased to some extent. Here, the decreasing of AAEM content and the presence of coal ash in the regenerated ash were proven by energy dispersive X-ray spectroscopy/EDX analysis (SEM/EDX SU 6600, Hitachi, Japan). EDX analysis was employed here since the available amount of sample was limited and the XRF analysis was not applicable. As shown in Table 5, AAEM content in the recovered BS ash was decreased from 65.6 to 64.1 wt% after the first regeneration and further decreased to 61.2 and 59.4 wt% for the second and the third regenerations, respectively. AAEM content in the recovered EG ash was also detected decreased from 73.1 wt% to 69.0, 72.3, and 67.6 wt% for the first, second, and third regenerations, respectively. In contrast, Si and Al contents in the recovered EG ash were increased to some extent due to the presence of coal ash in the regenerated ash. For BS ash, Al species was only detected in the second, and third regenerated ashes and Si was not detected in all ash samples.

Fig. 5 also shows that the catalytic activity of EG ash was more stable than BS ash even though its activity was a little lower. The stability difference of the EG and BS ashes was mainly due to the difference of potassium content in them. As shown in Table 3, BS

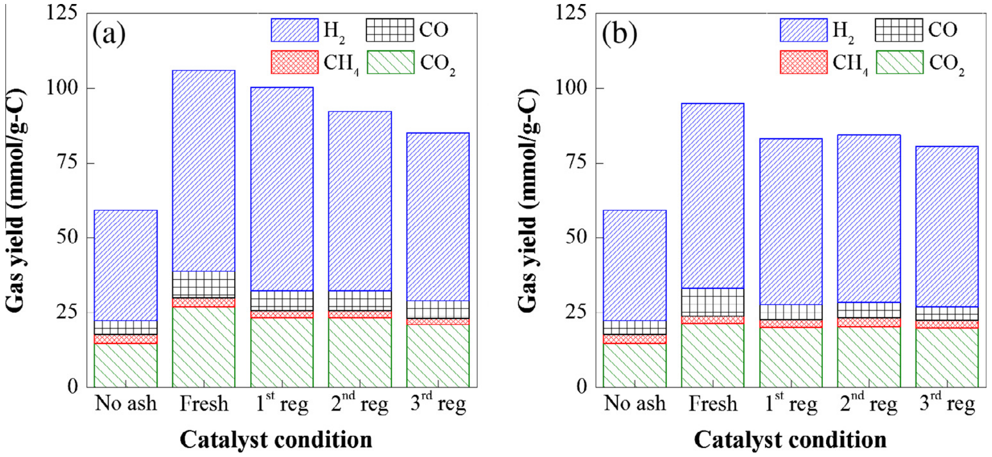

Fig. 5. Reusability test for BS (a) and EG (b) ashes when the weight amount of the regenerated ash was maintained.

Table 5
AAEM contents in the regenerated BS and EG ashes based on EDX analysis.

	Metal content (wt%)					
	K	Ca	Mg	Total AAEM	Si	Al
BS ash						
Fresh	23.2	27.6	14.8	65.6	–	–
1st regenerated	21.0	26.0	17.1	64.1	–	–
2nd regenerated	17.7	27.3	16.2	61.2	–	3.6
3rd regenerated	17.4	19.4	22.6	59.4	–	3.3
EG ash						
Fresh	5.1	52.6	15.7	73.4	4.4	–
1st regenerated	–	53.5	15.5	69.0	5.0	2.1
2nd regenerated	–	56.6	15.7	72.3	6.0	4.0
3rd regenerated	–	51.1	16.5	67.6	6.6	4.3

ash contained higher amount of potassium so that it had higher catalytic activity than EG ash. However, potassium seemed to be more volatile than alkaline earth species such as calcium and magnesium. It was proven by the EDX result for BS ash presented in Table 4 which shows that potassium species was gradually decreased along with the increase in regeneration times. The decreasing of potassium content in the BS ash led to the decrease in its catalytic activity. In the case of EG ash, K species was only detected in the fresh ash and no more K species left in the regenerated one. Thus, only alkaline earth species left in the ash along with other metal species. Since the amount of alkaline earth species were relatively stable in the regenerated EG ash, its catalytic activity was also observed to be more stable than BS ash.

Based on the above discussion, it is suggested that the stability of the ash could be improved by maintaining the content of AAEM in the regenerated ash rather than maintaining the weight amount of ash itself. In the present study, more fresh ash was added to the recovered ash so that the total AAEM amount in the regenerated ash remained as the same as that in the fresh one (Table 4). Simple arithmetical calculation was performed to determine the fresh ash needed by combining the ash content data presented in Table 3 for the fresh ash and Table 5 for the regenerated ash. Fig. 6 shows the results of stability test for BS and EG ashes when the amount of AAEM in the regenerated ash was maintained nearly as the original one. Compared with the results in Fig. 5, the catalytic stability was improved, and the gas yield kept at more stable state. However, a slight decrease of the gas yield was still observed even in the case of maintaining the AAEM amount. This should be mainly caused by the presence of silica, which came from the coal ash, in the regenerated ash.

4. Conclusions

The possibility of utilizing biomass ash as the catalyst to improve the steam gasification rate for low-rank coal was investigated. It is found that different biomass ashes had different catalytic activities. For the selected three kinds of biomass ashes, brown seaweed and eel grass ashes with high content of AAEM species showed better catalytic activities. Rice straw ash with high silica content showed almost no promoting effect on the gas production rate. The catalytic activity of the ash was strongly

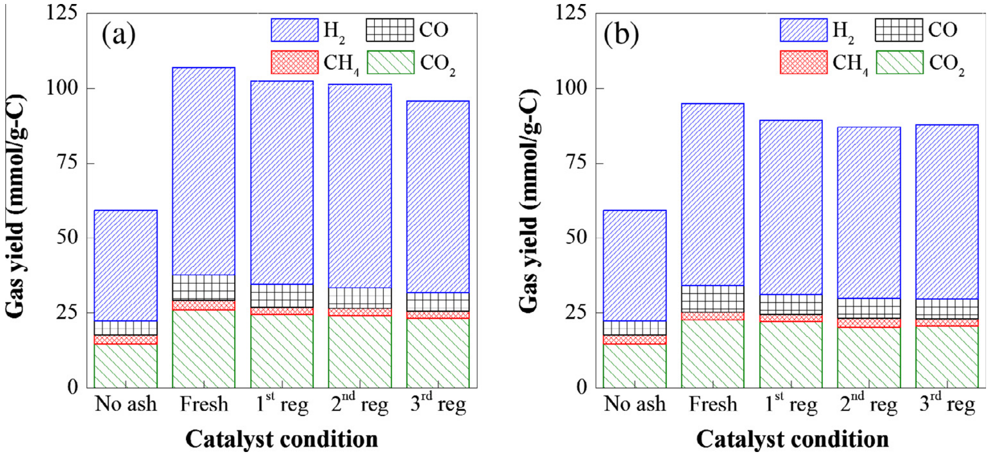

Fig. 6. Stability test for BS (a) and EG (b) ashes when the content of AAEM in the regenerated ash was maintained.

determined by the AAEM content in the ash and higher AAEM content resulted in higher catalytic activity. However, the presence of silica decreased the catalytic activity of the ash. This was also identified by using the simulated catalysts. All in all, biomass ash with high content of AAEM and low content of silica can be applied as a low cost gasification catalyst.

Acknowledgments

This study is supported by Strategic International Collaborative Research Program (SICORP), Japan Science and Technology (JST), and Aomori City Government, Japan. The authors would like to thank Dr. Yutaka Kasai at Aomori Prefectural Industrial Technology Research Center for his technical support on experiments, and Professor Koyo Norinaga at Kyushu University and Dr. Koichi Matsuoka at National Institute of Advanced Industrial Science and Technology (AIST, Japan) to provide coal samples. J. Rizkiana and B.W. Wahyu gratefully acknowledge the scholarship from Ministry of Education, Culture, Sport, Science, and Technology (MEXT) of Japan.

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